

## USE OF SELF-PROPAGATING CRYSTALLIZATION PHENOMENON IN THE PRODUCTION OF GLASS CERAMIC MATERIALS

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The possibility of using self-propagating crystallization accompanied by the propagation of the crystallization heat wave front in the transition of foam silica produced on the basis of compositions in the system  $\text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$  by the reducing melting method with melt separation and subsequent cooling of the silicate component under a thermal shock from the x-ray-amorphous state to the crystalline state is studied. The characteristics of the thermal wave are identified, the dependence of the velocity of propagation of the thermal wave on the dispersion of the foam silicate and molding pressure is established.

The thermal analysis method is used to determine the enthalpy of chemical reactions and phase transformations as well as the kinetic parameters of homogeneous and heterogeneous reactions under non-isothermal heating [1, 2].

The purpose of our study is to investigate the possibility of using the heat wave energy of self-propagating crystallization (SC) arising as a result of a physical transformation (phase transition) for production of glass ceramic materials.

X-ray-amorphous products for study were prepared on the basis of compositions in the  $\text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$  system according to the methods proposed by the authors in [3, 4] (RF Patents Nos. 2132306 and 2192397).

Initial materials were vermiculite from the Tatarskoe deposit (Krasnoyarsk Region) and lime, whose chemical compositions are listed in Table 1.

The batch prepared was melted in a reducing medium separating the melt into metallic and silicate components; then the silicate component of the melt was cooled using a thermal shock by discharging it into water. The “metallic” component was discharged separately. The resulting x-ray-amorphous foam silicate was milled to a size of 80 and 40  $\mu\text{m}$ ; next, two series of products with a diameter of 10 mm

and height 18 mm were molded under different pressures within the range of 50–350 MPa. The articles were heat-treated, and differential thermal analysis curves recorded. The heating rate of the furnace was 4.88 K/sec. In recording thermal analysis curves, the reference standard was the material studied by us. Junctions of a differential thermocouple were placed at different heights. The distance between the thermocouple junctions was set equal to 6 mm.

DTA curves were recorded as follows. Two holes of diameter 0.2 mm were drilled in an article analyzed at a symmetric distance of 4 mm from the center of the article to a depth of 12 and 6 mm. Next, junctions of chromel-alumel thermocouples were inserted in the holes in the lower end of the articles, and the articles were vertically placed into the furnace. The zero thermocouple junction was placed into a vessel with ice, which ensured a temperature equal to 273 K. The free ends of the thermocouples were connected to a recorded, whose strip chart velocity was set equal to  $4 \times 10^{-4}$  m/sec. The temperature in the furnace was recorded after each 323 K on the strip chart.

After thermal treatment the glass ceramic obtained was analyzed on a DRON-3 diffractometer using  $\text{CrK}_\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) in the interval of  $2\theta$  (5–70°) for the purpose of identifying its crystallographic structures. The com-

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TABLE 1

Initial material	Mass content, %								
	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{SO}_3$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	calcination loss
Vermiculite	38.82	9.28	16.54	2.55	18.34	0.22	0.46	5.15	8.64
Lime	2.64	0.64	0.33	59.16	–	0.04	0.07	0.40	36.72

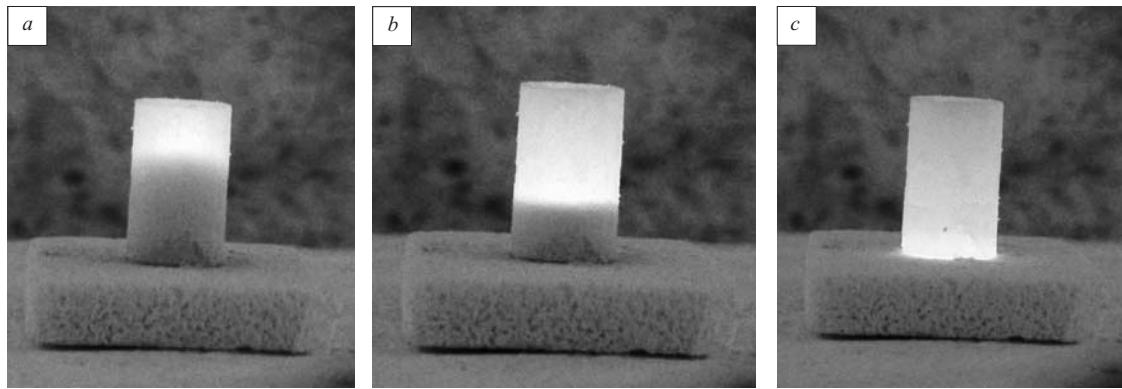


Fig. 1. SC heat wave front at the moment of passing the upper (a) and the lower (b) junctions of the thermocouple and the end of SC heat wave propagation (c).

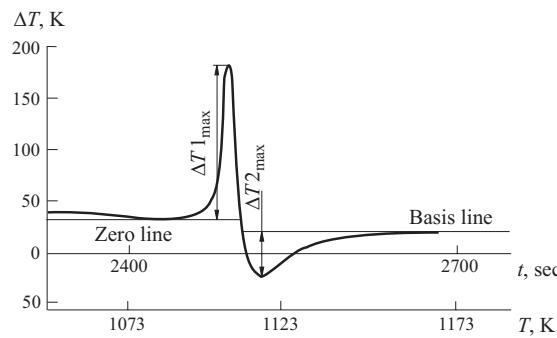


Fig. 2. Structure of SC heat wave front of x-ray-amorphous foam silicate of system  $\text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ .

pressive strength of the material was measured according to the standard method on a IR 5047-50-03 test breaking machine.

As the furnace reaches a quasistationary regime, the basis line goes parallel to zero line, except for the temperature intervals of phase transformations.

When the furnace is heated to 1088 K, a narrow brightly luminescent high-temperature zone is formed in the upper part of the product, in which the material transforms from an amorphous state to the crystalline state. The heat released by this zone is transmitted to the adjacent layer of amorphous material. If the heat is sufficient for heating the neighboring layer to a point of transformation (phase transition), the process propagates along the sample in the form of a heat wave front of SC, similarly to the phenomenon of self-propagating high-temperature synthesis in which a thermal wave is maintained by chemical transformation heat [5]. When the heat wave front approaches the upper junction of the differential thermocouple (Fig. 1a, furnace temperature 1106 K), a peak emerges on the thermal analysis curve directed upwards from the basis line. The temperature difference between the differential thermocouple junctions at this moment reaches a maximum value  $\Delta T_{1\max}$ . After the wave front passes over the upper junction of the thermocouple, the temperature of the

upper part of the product starts decreasing. When the temperatures of the upper and lower junctions of the thermocouple become equal, the current changes its direction. As the heat wave front approaches the second junction of the thermocouple (Fig. 1b), a peak arises on the DTA curve directed downwards from the basis and zero lines. At that moment the temperature difference between the junctions of the thermocouple reaches a maximum value  $\Delta T_{2\max}$  as well. The process of self-propagated crystallization lasts about 300 sec. The time of covering the distance between the thermocouple junctions is 27.5 sec. After the heat wave front passes through the article (Fig. 1c), its brightness for several seconds is higher than the brightness inside the furnace volume. During this time span the descending branch of the curve approaches the basis line and the temperatures of the article and the furnace become leveled. This time characterizes the thermal inertia of the device and depends on the thermal resistance and heat capacity of the product.

A typical structure of a SC wave (thermal analysis curve) is shown in Fig. 2, in which the process duration  $t$  is measured along the abscissa axis based on the strip chart velocity and an Endim 621.02 recorder and the strip chart length, as well as the furnace temperature  $T$ , whereas the difference in the temperatures of the upper and lower thermocouple junctions  $\Delta T$  is measured along the ordinate axis. It can be seen that the heat emission peaks are not symmetrical and the basis lines of the peaks are not located on the same straight line. The temperature variation rate in the upper part of the curve reaches 9.55 K/sec, whereas in the lower part it is 7.22 K/sec. The phenomenon observed is related to the different thermal conductivity of the material investigated in the amorphous and in the crystallized states divided by the SC wave front, which changes heat transfer conditions inside the product and affects the curve shape. The effect of heat transfer from the furnace to the article and heat transfer inside the thermocouple are insignificant in view of the virtually isothermal conditions of the process.

The flat top of the lower DTA peak shows that the thermal wave front velocity decreases. This is indicated as well

by a change in the ascending branch angle of the lower peak. It should be noted that as the molding pressure increases, the surface areas under the upper and the lower peak curves become redistributed proportional to the heat of phase transformations: with increasing pressure the surface area under the lower peak curve increases, whereas the surface area under the lower peak curve decreases. This may be due to the formation of a gaseous phase (gas adsorbed in material pores) in front of the SC heat wave, and the quantity of the gaseous phase growing, as the heat wave front moves downwards. In denser materials emission of gas is impeded, and its presence in front of the crystallization wave restricts the heat exchange in the material between the thermocouples inside the article, which may result in increasing the surface area of the peak under the lower DTA curve and decreasing the thermal conductivity of the material.

Calculations of phase transformation heat were carried out in accordance with the data in [1] based on the equation

$$m\Delta H = k \int_{t_1}^{t_2} \Delta T dt,$$

where  $m$  is the weight of the article, g;  $\Delta H$  is the phase transformation heat, J;  $k$  is the heat transfer coefficient,  $W/(m^2 \cdot K)$ ;  $\Delta T$  is the temperature difference between the differential thermocouple junctions, K;  $t$  is the time, sec.

The expression under the integral  $\Delta T dt$  characterizes the surface area of the peak under the curve. The heat of phase transformation in the transition from an amorphous state to a crystalline state was calculated using the method of weighing surface areas of the reference material (NaCl) and the material investigated. As molding pressure varied from 50 to 350 MPa, the heat of phase transformation varied insignificantly from 200 to 220 kJ/g.

The velocity of the heat wave front was determined based on the distance specified between the differential thermocouple junctions and the time taken to pass this distance calculated from the strip chart velocity (the time between the curve peaks). The dependence of the velocity of the self-propagated crystallization wave front on molding pressure is shown in Fig. 3. It can be seen that the velocity of the SC wave front depending on molding pressure varies insignificantly and is linear. With a maximum molding pressure (350 MPa), the velocity of the wave front is equal to  $2.66 \times 10^{-4}$  m/sec. Milling of amorphous foam silicate to a finer fraction (40  $\mu$ m) leads to a slight increase in the velocity of the thermal wave front.

The results of x-ray phase analysis of crystallization products identify the presence of a single phase, i.e., helenite,

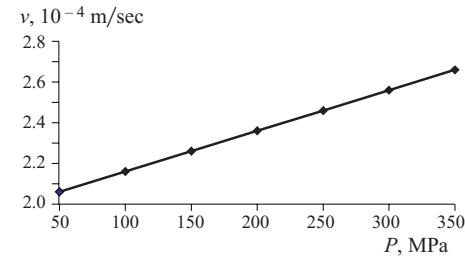


Fig. 3. Dependence of the velocity of SC wave front propagation  $v$  on molding pressure  $P$  of foam-silicate products.

and do not depend on molding pressure. The absence of structures containing magnesium oxide points to its presence in the residual vitreous phase, which is corroborated by chemical analysis data. The vitreous phase acts as a binder in articles [6]. This ensures high mechanical strength of articles heat-treated in the mode of self-propagating crystallization. The compressive strength of material obtained depending on molding pressure ranges from 40 to 160 MPa.

Thus, the process of self-propagating crystallization in the transition of an x-ray-amorphous foam silicate obtained on the basis of compositions of the  $\text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$  system into a crystalline state, which is manifested in the form of a heat wave front, can be used in the production of glass ceramic materials. The use of the effect of self-propagating crystallizing allows for a significant decrease in duration and temperature of heat treatment. The glass ceramic material obtained has the helenite structure and a compressive strength from 40 to 160 MPa depending on milling dispersion of the foam silicate and molding pressure.

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